Classification
Physics Abstracts
68.55B — 79.60 — 61.10

In-situ surface technique analyses and *ex-situ* characterization of $Si_{1-x}Ge_x$ epilayers grown on Si(001)-2 × 1 by molecular beam epitaxy

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(*Received 15 November 1993, accepted 4 January 1994*)

Résumé. — Des couches minces d'alliage $Si_{1-x}Ge_x$ épitaxiées à 400 °C sur des substrats Si(001) sont caractérisées *in situ* par des techniques d'analyse de surface telles que la spectroscopie de photoélectrons X et ultraviolet (XPS, UPS), la diffraction d'électrons lents (LEED) et la diffraction de photoélectrons (XPD). Les concentrations de germanium en surface déterminées à partir des rapports d'intensité des niveaux de cœur du germanium et du silicium sont systématiquement supérieures à celles obtenues à partir des flux d'évaporation. Ce résultat indique un enrichissement en germanium des couches proches de la surface, confirmé par l'obtention de spectres UPS similaires à ceux du germanium massif. Les résultats de LEED et ceux obtenus par XPD confirment la structure cristallographique des couches dans la mesure où les variations angulaires de l'intensité des pics Auger LMM du germanium et Si2p du silicium dans l'alliage sont identiques à celles du silicium (001). La contrainte résiduelle dans la couche est déterminée par diffraction de rayons X qui, comme la RBS, permet d'accéder à la concentration de l'alliage en germanium.

Abstract. — $Si_{1-x}Ge_x$ epilayers grown by Molecular Beam Epitaxy on Si(001) at 400 °C have been analyzed *in-situ* by surface techniques such as X-ray and Ultraviolet Photoelectron Spectroscopies (XPS and UPS), Low Energy Electron Diffraction (LEED) and photoelectron diffraction (XPD). The Ge surface concentrations (x) obtained from the ratios of Ge and Si core level intensities are systematically higher than those obtained by the respective evaporation fluxes. This indicates a Ge enrichment in the first overlayers confirmed by Ge-like UPS valence band spectra. The structured crystallographic character of the epilayers is ascertained by LEED and XPD polar scans in the (100) plane since the Ge Auger LMM and the Si 2p XPD intensity patterns from the $Si_{1-x}Ge_x$ epilayers are identical to those of the Si substrate. The residual stress in the epilayer is determined by *ex-situ* X-ray diffraction (XRD) which also allows, as Rutherford Back Scattering (RBS), Ge concentration determinations.

1. Introduction.

Silicon and germanium alloys show special promise in the growth of high performance devices in the silicon based technology due to the ability to grow pseudomorphic $Si_{1-x}Ge_x$ (or SiGe) epilayers on silicon. The main reports on the SiGe epilayer characterizations are devoted to *ex-situ* analyses and not so much works are done in conjunction with *in-situ* analyses. In this work, the SiGe epilayers grown by Molecular Beam Epitaxy (MBE) are investigated with a combination of *in-situ* surface techniques such as XPS, UPS and LEED and *ex-situ* characterizations namely XRD and RBS. These techniques allow comparison of Ge fractions (x) determined either by the angular shifts of the (004) SiGe X-ray diffraction line, or by the respective Ge and Si growth rate determination by quartz crystal monitoring, or also computed from XPS Si 2p and Ge 3d core level intensities or deduced from the RBS profiles. Owing to the more surfacial character of the Ge composition obtained by XPS, informations about surface segregation may thus be reached in conjunction with the more qualitative UPS and LEED investigation. Moreover, angle resolved electron detection of the XPS Si 2p or Auger LMM levels allows us to present the first X-ray photoelectron (XPD) or Auger Electron Diffraction (AED) patterns concerning SiGe alloys. These techniques give a direct image of the crystalline symmetry and also of the atomic rows in the topmost atomic layers of the alloy [1].

2. Experiment.

The *in-situ* experiments are carried out in an ultra high vacuum equipment consisting of an analyzing chamber fitted with LEED, XPS and UPS (operating at 1 253.6 eV and 21.2 eV source energies) and a MBE chamber. In both vessels, connected by a sample translation system, the pressure is near 10^{-10} mbar. The Si and Ge vapour fluxes, obtained by means of electron gun and Knudsen cell, respectively, are calibrated by two quartz crystal balances. The real evaporation rate is measured by a movable balance placed before the growth at the place of the substrate. The other remains always at a given place in the evaporation cones and checks the rate constancy during the process. Thus, the usual errors linked to the geometrical corrections, when quartz and sample do not see the same fluxes, are minimized.

The silicon substrate, cut along the [100] azimuth from a (001) silicon wafer, is mounted on a substrate-holder allowing a direct Joule heating and polar rotations around the translator axis coinciding in our geometry with the [100] crystal axis. It makes possible to change the polar angle θ between the normal to the surface and the electron emission direction and to probe comparatively the atomic arrangements in the crystallographic (100) plane of the substrate and of the deposited overlayer. The substrates are cleaned, *in-situ*, by Ar^+ sputtering cycles followed by annealing at 800 °C. This procedure generates Si(001) 2×1 reconstructed surfaces characterized by the well-known UPS surface state feature located at 0.8 eV below the Fermi level and attributed to the dimer dangling bonds and by the usual 2×1 LEED patterns.

Prior to the SiGe growth at 400 °C, a Si buffer layer of about 500 Å is systematically deposited at 600 °C on the preceding cleaned surface improving the quality of the starting surface as checked by relevant increases of the UPS surface state intensity and of the LEED spot brightness. The $Si_{1-x}Ge_x$ growth rates are typically between 0.3 and 0.5 Å/s. As abundantly reported in the literature, the critical thickness of pseudomorphic growth depends both on the substrate temperature T_s and on the Ge content [2, 3] for a deposition process with a given low contamination uptake. Owing to our low T_s used, which limits the islanding [4], and to the Ge composition range of the epilayers, we may expect a critical thickness of several hundreds of angströms.

The X-ray analyses are performed with a double crystal diffractometer at room temperature.

The measurement accuracy of the distance (d) between the observed crystalline planes is estimated at $4 \times 10^{-5}\, d$.

The RBS measurements are performed using a He^+ beam of 2 MeV and channeling is investigated with the beam along the [001] axis.

3. Results.

Figure 1 shows the first XPD patterns performed on SiGe alloys and allows us to compare them to the same polar scan from the Si buffer layer in the (100) high symmetry plane. This structural signature was already discussed and used in previous reports [5-7].

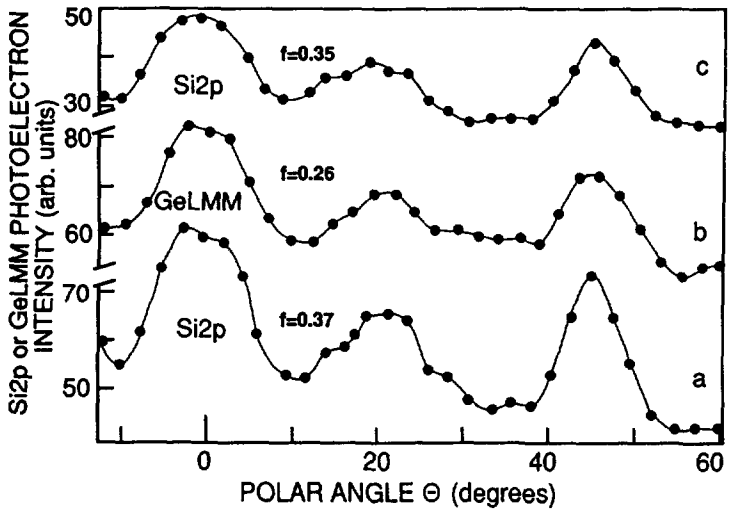

Fig. 1. — Experimental polar angle intensity distributions of (a) the Si 2p core level from a clean Si(001) buffer layer in the (100) plane, (b) the Ge LLM and (c) Si 2p components of the $Si_{1-x}Ge_x$ (sample 4 in Tab. I). The Si 2p contribution (c) originates exclusively from the Si of the alloy as its thickness is well above the electron escape depth and hence, the substrate contribution is completely attenuated.

The main peaks at $\theta = 45°$ and $\theta = 0°$ correspond to the expected electron forward scattering reinforcement [1] along the first and second neighbour atomic rows of the fcc array in the (100) plane. The substrate pattern (Fig. 1a) used as a signature of this atomic arrangement, is now compared to the very similar ones obtained from the Ge (Fig. 1b) or Si (Fig. 1c) atoms in the SiGe overlayer. These patterns correspond to a 265 Å SiGe epilayer (sample 4 in Tabl. I) whose thickness, one order of magnitude higher than the electron mean free path, ensures a complete attenuation of the substrate signal. Actually, XPD informations are limited to some tens of angströms upon the alloy surface. The pattern similarity between the substrate and the SiGe layer proves the same structural ordering in these materials. The peak contrasts [5-7] $f = \Delta I / I_{max}$, indicated in figure 1, may provide an estimation of the crystalline quality. ΔI is defined as the intensity variation between the peak maximum I_{max} (for instance at $\theta = 0°$) and the first signal minimum. We can reasonably admit that the epitaxy approaches the substrate perfection when the alloy factor f is close to the substrate value. We observe a very slight decrease of the contrast for Si in the epilayer compared to that of the substrate. It is more pronounced and significant for Ge. The reason of these decreases,

which might be attributed to growth defects, to the surface disorder due to the germanium segregation, or to the alternance of Si and Ge diffusers in the atomic rows, remains unclear. The polar-angle resolution as well as the measurement precision do not allow the observation of the weak angle decrease between the nominal [001] and [011] directions in the substrate ($\theta = 45°$) and in the strained alloys as done by Chambers and Loebs for Ge coverage on Si(001) [8]. Actually, this angle reduction, depending on the Ge content in the alloy, must be a correlated fraction of that observed by these authors for a strained Ge overlayer on Si(001) ($\Delta\theta = 1.1 \pm 0.2°$).

The *in-situ* and *ex-situ* characterizations allow determinations of the Ge concentration in the epilayers. These values deduced from the relative Ge and Si vapour fluxes (x_Q), from the XPS Ge 3d and Si 2p intensities recorded at two different emission angles 0° and 50° (x_{XPS}) or from *ex-situ* XRD measurements (x_{XRD}) are summarized in Table I. While the XRD determined composition fits well the quartz balance determination for samples whose thicknesses are lower than the critical thickness, we notice quasi systematically higher values for XPS determined compositions. Moreover, the values obtained at glancing emission angle (50°) which analyses the topmost layers of the alloy, are also somewhat higher than those obtained at normal emission corresponding to a more bulk-like analysis. These differences cannot be attributed to XPD signal variations since all Si and Ge elastic peaks follow similar angular variations as demonstrated in figure 1. A germanium enrichment at the alloy surface may explain the origin of these composition differences.

Table I. — *Characteristics of the investigated* $Si_{1-x}Ge_x$ *epilayers grown at* 400 °C, *namely the epilayer thickness estimated from the deposition rates given by the quartz monitoring and the* Ge *compositions of the alloy deduced from the relative vapor fluxes* (x_Q), *from the* XPS Si 2p *and* Ge 3d *intensities recorded at* 0° *and* 50° (x_{XPS}) *and from the X-ray diffraction measurements* (x_{XRD}).

Sample	Thickness (Å)	x_Q	x_{XPS} 0°	x_{XPS} 50°	x_{XRD}	Comments
1	390	0.062	0.092	0.102		
2	260	0.090	0.133	0.151		UPS
3	1 220	0.118	0.201	0.198	0.12	RBS (Fig. 4)
4	265	0.204	0.311	0.357		XPD (Fig. 1)
5	325	0.259	0.291	0.315	0.23	XRD (Fig. 3)
6	1 240	0.270	0.213	0.264	0.27	
7	3 200	0.276	0.477	0.486	0.40	
8	195	0.279	0.317	0.334		UPS (Fig. 2)

Due to its lower surface free energy, Ge has long been recognized to segragate in Si cap layers [9, 10] or in Si/SiGe and Si/Ge superlattices [11] grown by MBE. Our results show that this segregation does not only occur when Si is deposited on Ge substrates but also during co-deposition of these elements related to alloy growth in accordance with the general tendancy to minimize the free energy of the system.

This trend is further corroborated by the LEED patterns and valence band structures obtained by UPS (Fig. 2) which are still more surface sensitive techniques. The main argument consists of similar surfacial appearances of SiGe alloys and of Si surfaces covered by 1 or 2 monolayers of pure germanium both observed by LEED or by UPS. In these cases, the sharp 2×1 LEED structure of the Si surface, is replaced by a much more diffuse 1×1 surface

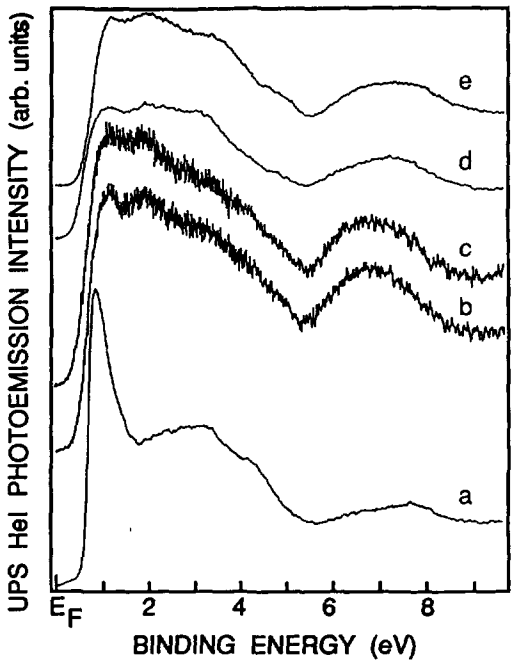

Fig. 2. — UPS HeI valence band photoemission spectra recorded at $\theta = 0°$ for (a) a clean Si(001)-2 × 1 surface of the buffer layer exhibiting the strong 2 × 1 dimer surface state and this Si buffer layer covered, (b) by one monolayer of germanium, (c) by two monolayers of germanium. Spectrum (d) corresponds to an $Si_{1-x}Ge_x$ epilayer with a low Ge concentration (sample 2 in Tab. I), (e) and an $Si_{1-x}Ge_x$ epilayer with a higher Ge concentration (sample 8 in Tab. I).

order. The XPD polar patterns, mainly similar for Si(001) 2 × 1 and SiGe(001) 1 × 1 surfaces (as determined by LEED), are probably only weakly affected by the surface reconstruction change. Indeed only the topmost layer is affected by this reconstruction change while the XPD information integrates the contributions of all atomic planes corresponding to the XPS probing depth (~ 23 Å or more than 15 monolayers). By UPS, the Si surface signature (Fig. 2a) characterized by the very strong dimer surface state at 0.8 eV below the Fermi level gives place to a more smooth triplet structure in the cases of silicon covered by germanium (Figs. 2b, c) or by $Si_{1-x}Ge_x$ alloys with different compositions (Figs. 2d, e). Besides a hump between 3 and 4 eV (probably a mixture of Si and Ge bulk states), the more structured features near 1.1 eV and 1.9 eV may be ascribed to Ge surface states [12]. These observations indicate that the top of $Si_{1-x}Ge_x$ alloy consists of nearly pure Ge layers or at least strongly enriched in Ge. Recently Butz and Kampers [13] arrived at a similar conclusion by Auger Electron Spectroscopy (AES) even if they observed more complicated LEED patterns depending on the SiGe thickness.

Double X-ray diffraction is an accurate method to determine the residual stress in the epilayers. This technique also allows the determination of the orientation as well as the crystalline quality of the epilayers. Using the Vegard's law for totally relaxed and also the Hooke's law for pseudomorphic epilayers, the germanium concentration is calculated taking into account the X-ray diffraction measurements. All the epilayers investigated with thicknesses up to 3 200 Å were monocrystalline with the orientation of the substrate.

Figure 3 presents a double X-ray diffraction rocking curve in logarithmic scale of a 325 Å thick SiGe epilayer grown on Si(001) with a $x_Q = 0.26$ value of Ge concentration (sample 5 in Tab. I). The (004) CuKα1 diffraction lines of the epilayer and of the substrate are observed at a

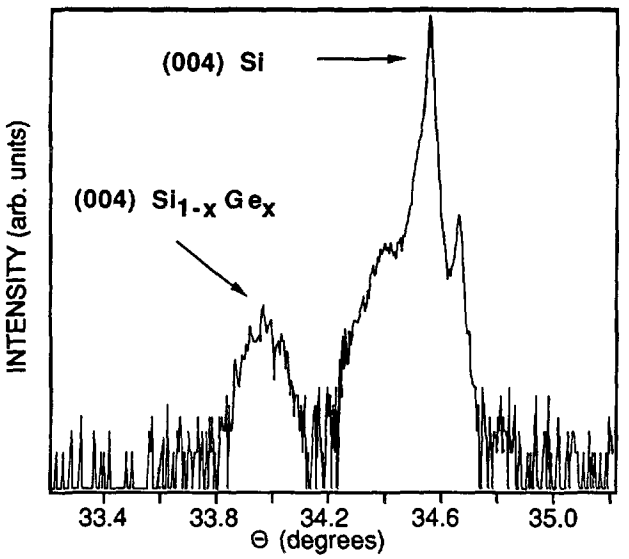

Fig. 3. — Double X-ray diffraction rocking curve of a 325 Å thick (sample 5 in Tab. I) $Si_{1-x}Ge_x$ epilayer grown on Si(001) with the intensity in logarithmic scale.

diffraction angle of 33.95 and 34.565°, respectively. Assuming that this epilayer is under elastic stress in this thickness range and taking into account the elastic constants of the SiGe material, the lattice parameter perpendicular to the interface ($a^{\perp}_{SiGe}$) is given by equation (1) :

$$a^{\perp}_{SiGe} = a_{Si} + (a_{SiGe} - a_{Si})\,[(2\,C_{12} + C_{11})/C_{11}] \quad (1)$$

where a_{Si} and a_{SiGe} are the lattice parameter of bulk Si and SiGe respectively, C_{11} and C_{12} are the elastic constants of the alloy calculated using a Vegard's law applied to the elastic constants of bulk materials [14]. In the concentration range from 0 to 50 percent, the factor depending of the elastic constant values in equation (1) does not vary more than 0.8 % and may therefore be considered constant at a value of 1.76. Using equation (1) and the experimental $a^{\perp}_{SiGe}$ value previously obtained (5.517 Å), the SiGe bulk lattice parameter is calculated and has a value of 5.479 Å. The germanium composition of the epilayer is then estimated, using the Vegard's law, at 0.23 which is in relatively fair agreement with the germanium concentration determined using the quartz monitoring (0.26). The stress (σ) in the epilayer is then calculated using equation (2)

$$\sigma = -\,[(C_{11} - C_{12})\,(C_{11} + 2\,C_{12})/2\,C_{12}]\,\varepsilon^{\perp} \quad (2)$$

where C_{ij} are the elastic constants of the SiGe bulk material and $\varepsilon^{\perp}$ is the strain perpendicular to the interface calculated using equation (3)

$$\varepsilon^{\perp} = (a^{\perp}_{SiGe} - a_{SiGe})/a_{SiGe}\,. \quad (3)$$

This 325 Å thick SiGe epilayer is under compressive strain parallel to the interface. Using equation (2), the stress is calculated and has a value of – 307 MPa. For a 1 220 Å thick SiGe epilayer (sample 3 in Tabl. I), with a Ge concentration $x_Q = 0.12$, the $a^{\perp}_{SiGe}$ was estimated at 5.4808 Å. Assuming that the epilayer is totally strained and using the same method as previously described, we obtained a SiGe lattice parameter value of 5.459 Å and a germanium

concentration of 0.12 in good accordance with *in-situ* measurements (see Tab. I). In this case the layer is under compressive strain parallel to the interface and the stress is estimated at – 157 MPa. The weak (004) SiGe diffraction peaks observed in linear scale for all the epilayers investigated with a thickness varying from 325 to 3 200 Å do not allow an estimation of the crystalline quality of the epilayer. This is attributed to the small value of the epilayer thickness and not to a low crystalline quality of the epilayer.

Figure 4 shows the RBS spectra of the preceding $Si_{1-x}Ge_x$ epilayer with a germanium concentration of $x_Q = 0.12$ (sample 3 in Tab. I) analysed with incident He^+ ions at an energy of 2 MeV. The crystalline quality (χ) of the epilayer is estimated using the ratio of the RBS intensities near the surface obtained in the channeling and in the random conditions. In this alloy χ is estimated at 5 % while an ideal Si(001) crystal should give a χ of 3 %. This difference between these values of χ indicates a lower crystalline quality of the epilayer in comparison with the crystalline quality of the Si(001) bulk material. The RBS measurements also allow the determination of the alloy concentration which is estimated at 0.11 in relatively good agreement with the composition obtained using XRD and the quartz monitoring (0.12).

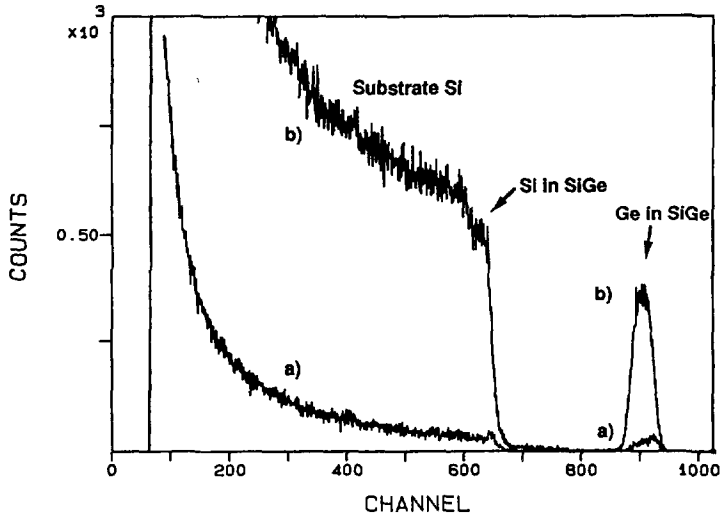

Fig. 4. — Rutherford back scattering spectra of a 1 220 Å thick $Si_{1-x}Ge_x$ epilayer (sample 3 in Tab. I) on Si(001) with a germanium concentration of $x_Q = 0.12$ (a). The lower spectrum (a) is taken with [001] channeled incidence and the upper spectrum (b) with random incidence.

4. Conclusion.

In summary, SiGe strained alloys with thicknesses up to 1 200 Å and with a Ge content up to 0.27 have been grown at a substrate temperature as low as 400 °C. *In-situ* surface studies have demonstrated the occurrence of a Ge segregation at the alloy surface. These $Si_{1-x}Ge_x$ epilayers were also probed, for the first time, by UPS and X-ray photoelectron diffraction.

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